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1 **Modelling the dispersion and transport of reactive pollutants in** 2 **a deep urban street canyon: Using large-eddy simulation**

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8 **Abstract:**

9 This study investigates the dispersion and transport of reactive pollutants in a deep urban street
10 canyon with an aspect ratio of 2 under neutral meteorological conditions using large-eddy
11 simulation. The spatial variation of pollutants is significant due to the existence of two unsteady
12 vortices. The deviation of species abundance from chemical equilibrium for the upper vortex is
13 greater than that for the lower vortex. The interplay of dynamics and chemistry is investigated using
14 two metrics: the photostationary state defect, and the inferred ozone production rate. The latter is
15 found to be negative at all locations within the canyon, pointing to a systematic negative offset to
16 ozone production rates inferred by analogous approaches in environments with incomplete emission
17 mixing. This study demonstrates an approach to quantify parameters for a simplified two-box
18 model, which could support traffic management and urban planning strategy or personal exposure
19 assessment.

20 **Capsule:**

21 Reactive pollutants in a deep street canyon exhibit significant spatial variation driven by two
22 unsteady vortices. A method of quantifying parameters of a two-box model is developed.

23 **Keywords:**

24 Urban street canyon, Large-eddy simulation, Pollutant removal, Turbulence, Two-box model.

25 **1 Introduction**

26 The term “street canyon” describes a restricted space (poor air ventilation) with surrounding
27 buildings along both sides of the urban street. Vehicle emissions are dominant among various
28 anthropogenic pollutant sources in urbanized areas (Liu et al., 2005). A combination of vehicle
29 emissions and reduced dispersion caused by surrounding buildings could result in poor air quality at
30 the pedestrian level, thereby leading to associated public health effects for those exposed to such
31 environments (Solazzo et al., 2011). Understanding the dispersion and transport of reactive
32 pollutants in urban street canyons is important to effectively quantify – and develop policies to
33 mitigate – such impacts.

34 Various approaches have been undertaken over recent years to tackle the issue of air pollution
35 inside street canyons. The most fundamental approach is direct field measurement, which can
36 provide the first-hand and useful information. Examples of such approach include the studies by
37 Xie et al. (2003), Kumar et al. (2008) and Prajapati et al. (2009). However, there are several
38 disadvantages of field measurements, e.g. challenges to data interpretation, uncontrollable
39 meteorological conditions, low spatial coverage, and high expense. An alternative approach is
40 physical modelling, such as wind tunnels, e.g. Sagrado et al. (2002), Kovar-Panskus et al. (2002),
41 Park et al. (2004) and Michioka et al. (2011), and water channels, e.g. Caton et al. (2003), Jiang et
42 al. (2007) and Li et al. (2008a). Physical modelling offers the advantages of fully controlling testing
43 parameters and sampling points so as to provide useful data for the evaluation of numerical models.
44 However, there is a challenge for such models to replicate fully the large-scale atmospheric
45 turbulence of the real world due to the scale limitation. Another useful alternative approach is
46 numerical simulation (e.g. computational fluid dynamics, CFD). With rapid development of
47 advanced computer technology, CFD has become a useful tool to explore experimental flow and
48 pollutant dispersion problems (Chang, 2006), providing a complete view of distribution of flow and
49 pollutant fields at high-resolution in both time and space. The most comprehensive applications of
50 CFD have been based on Reynolds-averaged Navier–Stokes (RANS) equations and large-eddy

51 simulation (LES). RANS can only predict mean information about the flow and pollutant fields,
52 while LES also provides the turbulent information about unsteadiness and intermittency (Cai et al.,
53 2008).

54 The flow patterns in a street canyon under neutral meteorological conditions can be classified into
55 three main regimes (Oke, 1987): isolated roughness, wake interference and skimming flow,
56 depending on the aspect ratio (AR, the ratio of building height H to street width W). Skimming flow,
57 which has been the subject of several studies and will be further investigated here, normally occurs
58 in the regular street canyons ($0.7 < AR < 1.5$) and deep street canyons ($AR > 1.5$) (Murena et al.,
59 2009). A single primary vortex is formed within the regular street canyon (e.g. $AR=1$), which has
60 been extensively studied. Most studies only considered passive pollutants (i.e. non-reactive scalars).
61 However, vehicle emissions are chemically reactive, evolving on the timescale of typical canyon
62 circulation and residence times. Such chemical processes are expected to play a role in determining
63 abundance, alongside dispersion and transport, of reactive pollutants. Baker et al. (2004) introduced
64 simple NO_x - O_3 chemistry into a LES model and examined reactive pollutant dispersion and
65 transport inside a regular street canyon ($AR=1$). The concept of the photostationary state (PSS)
66 defect was introduced and served as a sensitive indicator of reactive mixing. Baik et al. (2007)
67 carried out a RANS model of a regular street canyon ($AR=1$) using the same chemistry as the study
68 by Baker et al. (2004). Both these studies showed that the chemistry is close to equilibrium within
69 the primary canyon vortex, but far from equilibrium at the canyon roof level where air exchange
70 between the canyon and the overlying background takes place. Kikumoto and Ooka (2012)
71 investigated the transport and dispersion of atmospheric pollutants within a regular street canyon
72 ($AR=1$) by using LES coupled with a bimolecular chemical reaction ($O_3 + NO \rightarrow \text{product}$). They
73 found that NO_x and O_3 have contrasted mechanism of transport and the correlation between the
74 reactants' concentration fluctuations strongly influences the reaction rates at the canyon roof level.
75 Kwak and Baik (2012) and Kwak et al. (2013) employed a RANS model coupled with the carbon
76 bond mechanism IV (CBM-IV) considering the chemistry of O_3 , NO_x and volatile organic

77 compounds (VOCs) in idealized street canyons (AR=1,2). They found that both O₃ and OH
 78 oxidation processes are of vital importance in the canyon-scale chemistry and that there are two
 79 counter-rotating vortices in the street canyon with AR=2. According to Li et al. (2009), there are
 80 multiple vortices within a deep street canyon, which may create very poor ventilation conditions for
 81 pollutants. Thus the dispersion of pollutants in a deep street canyon could be substantially different
 82 from the AR=1 case, very complex in terms of both dynamical and chemical processing, and
 83 deserves a thorough examination.

84 This study investigates the dispersion and transport of reactive pollutants in a deep urban street
 85 canyon (AR=2). The LES methodology coupled with a simple chemical mechanism is employed as
 86 described in Section 2. In Section 3, the results of the LES dynamical model are evaluated against a
 87 water-channel experiment, and the characteristics of reactive pollutant dispersion from the LES
 88 coupled with the simple NO_x-O₃ chemistry are presented. A two-box model framework is
 89 developed. Finally, the conclusions are presented in Section 4.

90 **2 Methodology**

91 **2.1 Numerical model**

92 **2.1.1 Flow equations**

93 The LES model employed here is OpenFoam v2.1.1 (OpenFOAM, 2012), in which incompressible
 94 flow and neutral condition are assumed. The filtered momentum equations and continuity equations
 95 are

$$96 \quad \frac{\partial \bar{u}_i}{\partial t} + \frac{\partial}{\partial x_j} \bar{u}_i \bar{u}_j = -\Delta P \delta_{i1} - \frac{\partial \bar{p}}{\partial x_i} - \frac{\partial \tau_{ij}}{\partial x_j} + \nu \frac{\partial^2 \bar{u}_i}{\partial x_j \partial x_j} \quad (1)$$

$$97 \quad \frac{\partial \bar{u}_i}{\partial x_i} = 0 \quad (2)$$

98 where the overbar ($\bar{\bullet}$) represents the filtered quantity, \bar{u}_i ($i=1,2,3$) are the filtered velocities, ΔP is
 99 the large-scale kinematic pressure difference, δ_{ij} is the Kronecker delta, \bar{p} is the filtered kinematic
 100 pressure, ν is the kinematic molecular viscosity and τ_{ij} represents the sub-grid scale (SGS)
 101 stresses, which are parameterised as follows:

$$102 \quad \tau_{ij} = -2\nu_{SGS}S_{ij} \quad (3)$$

$$103 \quad S_{ij} = \frac{1}{2}\left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i}\right) \quad (4)$$

$$104 \quad \nu_{SGS} = C_k k_{SGS}^{1/2} \Delta \quad (5)$$

$$105 \quad \Delta = (\Delta_1 \Delta_2 \Delta_3)^{1/3} \quad (6)$$

$$106 \quad \frac{\partial k_{SGS}}{\partial t} + \frac{\partial}{\partial x_i}(k_{SGS}\bar{u}_i) = 2\nu_{SGS}S_{ij}S_{ij} + (\nu + \nu_{SGS})\frac{\partial^2 k_{SGS}}{\partial x_i \partial x_i} - C_\varepsilon \frac{k_{SGS}^{3/2}}{\Delta} \quad (7)$$

107 where k_{SGS} is the SGS turbulent kinetic energy, Δ_i ($i=1,2,3$) are the local grid spacings and the
 108 modelling constants $C_k = 0.094$, $C_\varepsilon = 1.048$.

109 The study simulates the high Reynolds number ($\sim 10^6$) turbulent flow (see Section 2.2) in a deep
 110 street canyon with rough surfaces and the logarithmic law of the rough-wall (Schlichting and
 111 Gersten, 2000) is applied for the near-wall treatment:

$$112 \quad \bar{u}_\parallel = \frac{u_\tau}{\kappa} \ln \frac{z_\perp}{z_0} \quad (8)$$

113 where \bar{u}_\parallel is the resolved scale velocity component parallel to the wall, u_τ is the wall friction
 114 velocity, κ ($=0.42$) is the von Kármán constant, z_\perp is the distance normal to the wall and z_0
 115 ($=0.015$ m representing a characteristic physical length of 0.15 m, e.g. window frames) is the
 116 aerodynamic surface roughness length. u_τ is calculated by Equation (8) and used to derive ν_{SGS}
 117 near the wall using

$$118 \quad \nu_{SGS} = \frac{u_\tau^2}{|\nabla \bar{u}_\parallel \cdot \hat{n}|} - \nu \quad (9)$$

119 where \hat{n} is the unit vector normal to the wall.

120 2.1.2 Equations for reactive pollutants

121 The reactive pollutants concerned here are nitric oxide (NO), nitrogen dioxide (NO₂) and ozone
122 (O₃). The associated chemical reactions are (Carpenter et al., 1998):



126 where M denotes a third body molecule (usually O₂ or N₂) which absorbs excess energy so that O
127 and O₂ may recombine to form an O₃ molecule. The filtered equations for the concentrations of
128 reactive pollutants are:

$$129 \quad \frac{\partial [\overline{\text{NO}}]}{\partial t} + \frac{\partial}{\partial x_i} (\bar{u}_i [\overline{\text{NO}}]) = \frac{\partial}{\partial x_i} \left(\left[\frac{\nu + \nu_{SGS}}{Sc} \right] \cdot \frac{\partial [\overline{\text{NO}}]}{\partial x_i} \right) + J_{NO_2} [\overline{\text{NO}_2}] - k_1 [\overline{\text{O}_3}] [\overline{\text{NO}}] + S_{NO} \quad (13)$$

$$130 \quad \frac{\partial [\overline{\text{NO}_2}]}{\partial t} + \frac{\partial}{\partial x_i} (\bar{u}_i [\overline{\text{NO}_2}]) = \frac{\partial}{\partial x_i} \left(\left[\frac{\nu + \nu_{SGS}}{Sc} \right] \cdot \frac{\partial [\overline{\text{NO}_2}]}{\partial x_i} \right) - J_{NO_2} [\overline{\text{NO}_2}] + k_1 [\overline{\text{O}_3}] [\overline{\text{NO}}] + S_{NO_2} \quad (14)$$

$$131 \quad \frac{\partial [\overline{\text{O}_3}]}{\partial t} + \frac{\partial}{\partial x_i} (\bar{u}_i [\overline{\text{O}_3}]) = \frac{\partial}{\partial x_i} \left(\left[\frac{\nu + \nu_{SGS}}{Sc} \right] \cdot \frac{\partial [\overline{\text{O}_3}]}{\partial x_i} \right) + k_2 [\overline{\text{O}}] [\overline{\text{O}_2}] [\overline{\text{M}}] - k_1 [\overline{\text{O}_3}] [\overline{\text{NO}}] \quad (15)$$

132 where J_{NO_2} is the photolysis rate for NO₂ in Reaction (10); k_1 and k_2 are the rate constants for
133 Reactions (11) and (12), respectively; S_{NO} and S_{NO_2} are the emission rates for NO and NO₂,
134 respectively; Sc (=0.72) is the Schmidt number. Based on the pseudo-steady-state approximation for
135 the highly reactive oxygen atom (O) (Seinfeld and Pandis, 1998), the formation rate of O by

136 Reaction (10) is the same as the depletion rate of O by Reaction (11). Thus, the following equation
 137 is derived:

$$138 \quad k_2[\overline{O}][\overline{O_2}][\overline{M}] = J_{NO_2}[\overline{NO_2}]. \quad (16)$$

139 Therefore, substituting Equation (16) into Equation (15) yields:

$$140 \quad \frac{\partial[\overline{O_3}]}{\partial t} + \frac{\partial}{\partial x_i}(\overline{u_i}[\overline{O_3}]) = \frac{\partial}{\partial x_i} \left(\left[\frac{\nu + \nu_{SGS}}{Sc} \right] \cdot \frac{\partial[\overline{O_3}]}{\partial x_i} \right) + J_{NO_2}[\overline{NO_2}] - k_1[\overline{O_3}][\overline{NO}] \quad (17)$$

141 For further analysis, the photostationary state (PSS) defect d_{ps} (Baker et al., 2004) is defined:

$$142 \quad d_{ps}(\%) = \left(\frac{k_1[\overline{O_3}][\overline{NO}]}{J_{NO_2}[\overline{NO_2}]} - 1 \right) \times 100, \quad (18)$$

143 where the values of J_{NO_2} and k_1 are 0.0092 s^{-1} and $0.0004 \text{ ppb}^{-1} \text{ s}^{-1}$, respectively (Bright et al., 2013).

144 d_{ps} is a widely-used measure of the deviation from chemical equilibrium. The larger is the
 145 magnitude of d_{ps} , the higher is the deviation from the chemical equilibrium. $d_{ps} = 0$ means that the
 146 chemistry is at the equilibrium state.

147 We may also define PO_3 as the ozone production rate associated with the VOCs chemistry under the
 148 perfect mixing condition as follows. Atmospheric chemical reactions of hydro- and organic-peroxy
 149 radicals (HO_2 and RO_2) with NO generate NO_2 through:



152 Considering a chemical equilibrium system with perfect mixing comprising Reactions (10)-(12),
 153 (19) and (20), we obtain

$$154 \quad J_{NO_2}[\overline{NO_2}] - k_1[\overline{O_3}][\overline{NO}] = k_3[\overline{NO}][\overline{HO_2}] + \sum_i k_{4,i}[\overline{NO}][\overline{RO_2}]_i \quad (21)$$

155 where k_3 and $k_{4,i}$ are the rate constants for Reactions (19) and (20), respectively; i is the i^{th} organic-
 156 peroxy radical. The terms $k_3[NO][HO_2] + \sum_i k_{4,i}[NO][RO_2]_i$ represent the rate of conversion of
 157 NO to NO_2 (through the VOCs chemistry) which is subsequently photolysed leading to O_3
 158 production. Thus we define $PO_3 = k_3[NO][HO_2] + \sum_i k_{4,i}[NO][RO_2]_i$. Due to the difficulties of
 159 evaluating HO_2 and RO_2 from measurement, we may use (21) to infer PO_3 from the NO_x and O_3
 160 measurements:

$$161 \quad PO_3 = J_{NO_2}[\overline{NO_2}] - k_1[\overline{O_3}][\overline{NO}], \quad (22)$$

162 This is referred to as the NO_x - O_3 -steady-state-defect approach. In this approach, we assume that
 163 deviations from PSS arising from imperfect mixing are negligible (Volz-Thomas et al., 2003). We
 164 evaluate the accuracy of this assumption within the canyon environment in Section 3.2.1.

165 **2.2 Model configuration and initialisation**

166 Fig.1 illustrates schematically the computational domain of an idealised deep street canyon ($AR=2$,
 167 i.e. $H=36\text{ m}$ and $W=18\text{ m}$). The building width B is 18 m . The domain width sizes
 168 $(L_x \times L_y \times L_z)$ are $36\text{ m} \times 40\text{ m} \times 112\text{ m}$. The grid resolutions $(\Delta x \times \Delta y \times \Delta z)$ are $0.3\text{ m} \times 1\text{ m} \times 0.3\text{ m}$,
 169 with Δz gradually increasing from 0.3 m at the canyon roof level to a maximum value of 5.54 m at
 170 the top. The number of grid cells in the x -, y - and z -directions is $60 \times 40 \times 120$ within the canyon
 171 and $120 \times 40 \times 40$ above the canyon, respectively.

172 A constant pressure gradient (ΔP) across the free surface layer (above the canyon) is imposed in
 173 the x -direction to drive the atmospheric flow (perpendicular to the street axis), representing the
 174 worst-case scenario for the dispersion of reactive pollutants within a street canyon (Li et al., 2008b).
 175 The prevailing wind speed U_f is about 2.2 m s^{-1} and the Reynolds number $Re (= U_f H / \nu)$ is the
 176 order of 10^6 . For velocity components, the symmetry boundary condition is employed at the domain
 177 top. Cyclic boundary conditions are specified in both the x - and y - directions. Therefore, the model

178 configuration represents an infinite number of idealised street canyons along the x -direction and
179 each canyon is infinitely long in the y -direction, which is a good approximation of real street
180 canyons relevant to traffic management or urban planning.

181 Emissions sources are assumed to be two continuous line sources representing two lanes of traffic
182 located at 2.5 m from both sides of the canyon centre at $z=1$ m with a Gaussian distribution (i.e.
183 $\delta_x=3$ m and $\delta_z=1$ m) so that the near-vehicle dispersion is approximated. Drawing upon the UK
184 Road Vehicle Emission Factors (Boulter et al., 2009b), the emission rate of NO_x is determined as
185 $620 \text{ g km}^{-1} \text{ h}^{-1}$, which represents an urban continuous road traffic of 1500 vehicles h^{-1} with an
186 average speed of 30 mph for a fleet composition representing the year of 2010 (Zhong et al., 2014).
187 The total emission for NO_x applied here is equivalent to 1000 ppb s^{-1} released into a typical LES
188 model grid ($0.3 \text{ m} \times 1 \text{ m} \times 0.3 \text{ m}$) but this total emitted NO_x is re-distributed based on the Gaussian
189 distribution mentioned above. The ratio of NO to NO_2 emission rate is 9:1 by volume. The
190 background concentrations of NO, NO_2 and O_3 used are 3.07, 6.02 and 43.62 ppb (Bright et al.,
191 2013), respectively, which are uniformly distributed among the whole domain initially and also
192 employed as the inlet boundary conditions, i.e. signifying no emissions from upwind canyons. For
193 the outlet, the advective boundary condition (i.e. $\frac{\partial \bar{c}_i}{\partial t} + \bar{u} \frac{\partial \bar{c}_i}{\partial x} = 0$) is applied, representing no
194 reflection of pollutants back into the computational domain. For the solid boundaries, zero-gradient
195 boundaries are applied without considering the effect of pollutant deposition. The symmetry
196 boundary is set on the top boundary and a cyclic boundary condition is adopted in the y - direction
197 for the pollutants.

198 Initially, the LES model is run with dynamics only for 5 hours in order to generate a statistically
199 steady turbulent flow turbulent flow. We take the dynamical-equilibrium flow field as the initial
200 condition (i.e. $t=0$ min) for the model in this study and further run the LES model without
201 chemistry for the first 30 min before considering chemistry. At $t=30$ min, the chemistry scheme

202 and emissions modules are turned on for the next 210 min ($t = 30$ to 240 min) with a time step of
 203 0.03 s in order to reach chemical quasi-equilibrium. For the analysis, the simulation 3-D outputs
 204 over the last 60 min period ($t = 180$ to 240 min) at a time interval of 3 s are stored and post-
 205 processed to derive the resolved-scale turbulent statistics based on the averages over the period and
 206 along the y -direction. This temporal average over $t \in [t_1, t_2]$ and spatial average over $y \in [0, L_y]$ of
 207 any quantity $\bar{\phi}(=\langle\bar{\phi}\rangle+\phi')$ gives $\langle\bar{\phi}\rangle$, which is a 2D function of (x, z) :

$$208 \quad \langle\bar{\phi}\rangle(x, z) = \frac{1}{L_y(t_2 - t_1)} \int_{t_1}^{t_2} \int_0^{L_y} \bar{\phi}(x, y, z, t) dy dt \quad (23)$$

209 and the fluctuation component ϕ' is described as follows:

$$210 \quad \phi'(x, z) = \frac{1}{L_y(t_2 - t_1)} \int_{t_1}^{t_2} \int_0^{L_y} [\bar{\phi}(x, y, z, t) - \langle\bar{\phi}\rangle(x, z)] dy dt \quad (24)$$

211 **3 Results and discussion**

212 **3.1 Flow field**

213 A water-channel experiment (Li et al., 2008a) is employed to evaluate the performance of the
 214 current LES simulation with respect to the flow field. This water-channel experiment was
 215 conducted in a laboratory flume, which was 10 m in length, 0.3 m in width and 0.5 m in height.
 216 Several identical building blocks ($0.1 \text{ m} \times 0.3 \text{ m} \times 0.1 \text{ m}$ in the x -, y - and z - directions) were placed
 217 perpendicular to the flow with the street width of 0.05 m (i.e. AR=2). The laser Doppler
 218 anemometer technique was applied for the data acquisition of the velocities and turbulent statistics.

219 Fig. 2 shows the comparison of vertical profiles of the normalized averaged streamwise and vertical
 220 velocities and their fluctuation intensities at the upstream, centre and downstream locations for the
 221 deep street canon (AR=2) between the current LES simulation and the water-channel experiment.

222 All of the quantities in Fig. 2 are normalized by u_{norm} (the averaged value of $\langle \bar{u} \rangle$ at the height
 223 $1.0 \leq z/H \leq 1.1$). Fig 2a presents the mean streamwise velocity and there is clear evidence of a
 224 shear layer across the canyon roof level, at which strong wind shear strength is observed. Fig. 2b
 225 shows the vertical mean velocities and there is clear evidence of the complicated flow pattern: the
 226 clockwise vortex in the upper part of the canyon and the weak anti-clockwise vortex in the lower
 227 part of the canyon. The upper recirculation is created by the strong wind shear at the roof level and
 228 the lower recirculation is generated by a relatively weaker wind shear induced by the upper
 229 recirculation. Figs. 2c and 2d illustrate the intensity of resolved-scale fluctuations of the two
 230 velocity components, which display local maxima at the canyon roof level. These maxima may be
 231 caused by the instability of the wind shear-layer at the canyon roof level. As shown in Fig. 2, there
 232 are some small discrepancies between the current LES simulation and the water-channel experiment.
 233 The current LES simulation generally slightly underestimates all the quantities. There are several
 234 possible reasons for this. Firstly, due to the computational cost, a limited computational domain is
 235 employed in the current LES simulation, only representing eddies with sizes smaller than half of the
 236 domain width. However, eddies in the experiment are created by the vortex generators and there
 237 may be larger eddies which are not modelled in the LES simulation. Secondly, the grid mesh might
 238 not be fine enough across the shear-layer, and so some small eddies within the shear-layer and the
 239 momentum exchange caused by these small eddies might not be resolved. Finally, these
 240 discrepancies may be attributed to different averaging approaches. In the LES simulation, the
 241 temporal and spatial averaging approach is adopted to derive the flow quantities. In the experiment,
 242 these quantities were only measured on a middle vertical plane in the y- direction (Li et al., 2008a).

243 Fig. 3 illustrates the vortex structure in the current LES simulation compared with a wind tunnel
 244 experiment carried out by Kovar-Panskus et al. (2002). Both the model and experiment shows that
 245 there are two counter-rotating vortices formed within the deep street canyon ($AR=2$). This is a
 246 major difference from the single-vortex flow for a street canyon with $AR=1$ (e.g. Bright et al.,
 247 2013). The two-vortex mean flow was also found by other studies for $AR=2$ using RANS, e.g.

248 Kwak et al. (2013), but their RANS model generated a larger lower vortex than the one found in the
249 water tank experiment and in the LES result here. It is also noted that the upper vortex is centred
250 lower within the canyon compared with the experiment. Also, the centre of the lower vortex is
251 shifted downstream closer to the windward wall compared with that of the upper vortex both in the
252 model and experiment.

253 Overall, the current LES simulation agrees well with the experiments in terms of the velocities,
254 turbulent intensities and vortex structure, which provides confidence that the simulated dynamics
255 within the canyon is reasonable. However, there are currently no suitable water-channel or wind-
256 tunnel experiments to evaluate the dispersion of reactive species, especially in deep street canyons.

257 **3.2 Pollutant dispersion and transport**

258 **3.2.1 Spatial variation of reactive pollutants**

259 Figs. 4a-f depict contour plots of the spatially and temporally averaged mixing ratios of (a) $\langle \overline{NO} \rangle$,
260 (b) $\langle \overline{NO_2} \rangle$, (c) $\langle \overline{O_3} \rangle$, (d) $\langle \overline{NO_x} \rangle$, (e) $\langle \overline{O_x} \rangle$, and (f) $\langle \overline{NO} \rangle / \langle \overline{NO_2} \rangle$. The plots show the influence of
261 two primary vortices, which span the deep street canyon: the upper clockwise vortex, and the lower
262 anti-clockwise vortex. This influence was also found by Kwak et al. (2013) for the street canyon
263 with AR=2. In general, the spatial patterns of the quantities for the upper vortex resemble those for
264 the single vortex in a street canyon with AR=1, e.g. Baker et al. (2004), Baik et al. (2007), Bright et
265 al., 2013, Garmory et al. (2009), Tong and Leung (2012), and Kwak and Baik (2012). There also
266 exist two shear layers. The first one is at the canyon roof level with increasing turbulence from the
267 leeward (upwind) building to the windward (downwind), which traps NO_x emissions near the
268 leeward building, allows more exchange near the windward building and entrains O_3 into the
269 canyon toward the windward building. The other one is at the level of around $z/W=0.5$, which
270 allows the NO_x emissions generated at the ground level inside the lower vortex to intrude into the
271 upper vortex and the ambient O_3 inside the upper vortex to be entrained into the lower vortex. NO_x

272 and O_3 are allowed to mix and react with each other inside the two vortices in the presence of the
 273 two shear layers where exchanges take place. It is also noted that there is an accumulation of traffic
 274 emissions with a maximum value of about 1100 ppb for NO_x and a low level of O_3 with a minimum
 275 value of about 4 ppb in the lower vortex. This is attributed to a high level of NO_x emitted into the
 276 very weak lower vortex to react with the limited O_3 entrained along the windward wall from above.
 277 This is very different from what Kwak et al. (2013) showed in their Fig. 2(d) which gives a local
 278 maximum of about 30 ppb near the centre of the lower vortex. One explanation is that their
 279 emission rate of NO_x is much lower than ours (20 vs. 90 ppb s^{-1} released into 1 m^3). Considering
 280 the NO_x - O_3 photochemistry, $NO_x = (NO + NO_2)$ and the total oxidant $O_x = (O_3 + NO_2)$ are
 281 effectively passive, exhibiting a similar spatial distribution to each other. The ratio of NO/NO_2 also
 282 shows a similar pattern across the two vortices ranging from about 6 at the right corner to about 3 at
 283 the canyon roof level, which indicates the conversion of NO to NO_2 by the within-canyon chemistry.
 284 Figs. 4g-h show contour plots of the spatially and temporally averaged d_{ps} and PO_3 . The
 285 magnitudes of d_{ps} and PO_3 are smaller in the lower vortex than that in the upper vortex indicating
 286 that there is greater mixing for the chemistry system to reach the chemical equilibrium in the lower
 287 vortex compared to that in the upper vortex. This can be explained by the weaker vortex in the
 288 lower part of the canyon, where time scale is adequate to approach chemical equilibrium. A local
 289 maxima in d_{ps} (about 150%) and PO_3 (about -0.68 ppb s^{-1}) are observed across the canyon roof
 290 level in the presence of the strong turbulence. It is also observed that there are significantly larger
 291 values of d_{ps} and PO_3 along the upper part of the windward building, indicating larger deviation
 292 from photochemical equilibrium in the region where two air parcels with very different chemical
 293 compositions interact.

294 Fig. 5 illustrates vertical profiles of (a) $\langle \overline{NO} \rangle$, (b) $\langle \overline{NO_2} \rangle$, (c) $\langle \overline{O_3} \rangle$, (d) $\langle \overline{NO_x} \rangle$, (e) $\langle \overline{O_x} \rangle$, (f)
 295 $\langle \overline{NO} \rangle / \langle \overline{NO_2} \rangle$, (g) d_{ps} and (h) PO_3 along the leeward and windward walls. These quantities are

296 averaged within the nearest three cells adjacent to the walls. The concentrations of NO, NO₂, NO_x,
 297 O_x and NO/NO₂ on the leeward wall are higher (around 1.5 to 2 times) than those on the windward
 298 wall within the upper part of the canyon, but lower (around 50% to 70%) within the lower part. This
 299 indicates that traffic emissions are mainly trapped within the anti-clockwise lower vortex. For O₃,
 300 the situation is reversed with much lower values on the leeward wall (around 6 ppb) compared to
 301 those on the windward wall (ranging from about 6 ppb to 20 ppb) within the upper part of the
 302 canyon, but with slightly higher values (about 2 ppb difference) within the lower part. This is
 303 attributed to ambient O₃ being brought into the upper part of canyon along the windward wall. It is
 304 also noted that the concentration reduces with height by a factor of about 0.8 on the leeward wall
 305 and by a factor of about 0.1 on the leeward wall for NO, NO₂, NO_x, O_x and NO/NO₂, but increases
 306 by a factor of about 1.3 on the leeward wall and by a factor of about 5.5 on the leeward wall for O₃.
 307 For the leeward wall, there is a sharp transition at the canyon roof level where each species rapidly
 308 approaches its background level, and a small gradient in concentration within the canyon. For the
 309 windward wall, there are two gradual transitions at the roof level and at the middle level of the
 310 canyon, respectively. These results for the upper part of the canyon match those of the field
 311 measurements by Xie et al. (2003), in which there was only one primary vortex inside the street
 312 canyon. The magnitudes of d_{ps} and PO_3 are very small (around 3% and 0.03 ppb s⁻¹, respectively)
 313 along the leeward wall inside the canyon, but increase rapidly within the shear layer at the roof level
 314 (around 80% and 0.40 ppb s⁻¹, respectively), where two air parcels with different compositions
 315 interact. Along the windward wall, the magnitudes of d_{ps} and PO_3 increase with height with much
 316 higher values in the upper part of the canyon, ranging from about 10% to 140% and from -0.08 ppb
 317 s⁻¹ to -0.53 ppb s⁻¹, respectively. This indicates that the deviation from chemical equilibrium is
 318 much larger in the upper vortex than that in the lower vortex.

319 Fig. 6 illustrates vertical profiles of the spatially and temporally averaged total, turbulent and
 320 advective fluxes, defined as $F_{total} = F_{turb} + F_{adv} = \langle w'\phi' \rangle(x, z) + \langle \bar{w} \rangle(x, z) \langle \bar{\phi} \rangle(x, z)$, for NO, NO₂, O₃,

321 NO_x , O_x and NO/NO_2 averaged across the canyon. It is interesting to note that the advective fluxes
322 are dominant for both the upper and lower vortices while turbulent fluxes are dominant for the shear
323 layers. It is observed that there is a positive (upward) total flux for NO and NO_2 from the canyon
324 roof level into the background atmosphere aloft, and a negative (downward) total flux for O_3
325 indicating that O_3 is brought into the canyon from the overlying background atmosphere. A rapid
326 increase in the total flux of NO and NO_2 is observed from the ground to the level at $z/W=0.1$. This
327 is due to the elevation of traffic emissions from the ground level. The total flux generally decreases
328 with height for NO , but increases for NO_2 indicating the conversion of NO to NO_2 within the
329 canyon chemical processing before they escape to the wider background environment. This
330 conversion is also indicated as the ratios of total fluxes of NO to NO_2 decrease with height from 9
331 near the emission source to about 4 at the canyon roof level. For the effective passive scalars NO_x
332 and O_x , the total fluxes generally remain almost constant with height (around 5 ppb m s^{-1} for NO_x
333 and 0.5 ppb m s^{-1} for O_x) except a rapid increase near the ground level.

334 In the model scheme used here, no peroxy radical reactions [Reactions (19) and (20)] are considered,
335 i.e. *net* chemical ozone production cannot occur. Non-zero values for d_{ps} , therefore reflect the
336 impact of imperfect mixing (heterogeneity) within the canyon, rather than ozone production
337 chemistry. The values of PO_3 obtained here may therefore be regarded as measures of a systematic
338 error in the NO_x - O_3 -steady-state-defect approach to assess ozone production rates (via NO_x/O_3
339 measurements in the real atmosphere), i.e. indicating the magnitude of the imperfect-mixing-
340 generated deviation from steady-state. The canyon averaged $PO_3 = -0.074 \text{ ppb s}^{-1}$ (i.e. -266 ppb h^{-1})
341 (see Fig. 4h) indicates a negative bias results at all locations, which is large compared with
342 measured free boundary layer / free troposphere ozone production rates [typically a few ppb h^{-1} , up
343 to 50 ppb h^{-1} in the most polluted regions, e.g. Mexico City (Wood et al., 2009)]. This reflects the
344 fact that the PO_3 term effectively represents a small difference between two large quantities, such
345 that the impact of mixing may be very substantial. In fact, this effect (imperfect mixing in the
346 vicinity of NO_x emission sources) is general, and so a systematic negative contribution to NO_x - O_3 -

347 steady-state derived ozone production rates will recur throughout the urban atmosphere, to an extent
348 dependent upon the local heterogeneity.

349 3.2.2 Development of a two-box model

350 The preliminary results from the LES model show the formation of two primary counter-rotating
351 vortices in the deep street canyon (AR=2), providing the potential to develop an alternative
352 simplified two-box model. By using a plane at the level of $z/W=0.5$ (or $z/H=0.25$), the deep street
353 canyon is divided into two boxes with the corresponding vortex inside each box (Figs. 3 and 7). It is
354 assumed that each vortex has sufficient intensity for the chemical species to be well-mixed within
355 the corresponding box (Murena et al., 2011). The mass transfer between two adjacent boxes is
356 expressed by the introduction of an ‘exchange velocity’. A one-box chemistry model has been
357 previously adopted by Liu and Leung (2008) to study reactive pollutant dispersion in street canyons
358 (AR=0.5, 1, 2), using the values of exchange velocity derived from LESs for different ARs.
359 Because they treated the whole canyon as one well-mixed box for all ARs, the model is unable to
360 reproduce the significant contrasts of pollutant concentration between the lower and upper canyon
361 as shown in Fig. 4. In this study, a more complex box model (i.e. a two-box model) is adopted:

$$362 \quad \frac{dc_{i,L}}{dt} = -\frac{w_{t,L}}{H_L}(c_{i,L} - c_{i,U}) + E_{i,L} + \Delta S_{i,L} \quad (25)$$

$$363 \quad \frac{dc_{i,U}}{dt} = \frac{w_{t,L}}{H_U}(c_{i,L} - c_{i,U}) - \frac{w_{t,U}}{H_U}(c_{i,U} - c_{i,b}) + \Delta S_{i,U} \quad (26)$$

364 where $c_{i,L}$, $c_{i,U}$ and $c_{i,b}$ are concentrations of i^{th} species ($i=NO$, NO_2 and O_3) in the lower box,
365 upper box and overlying background atmosphere, respectively; H_L and H_U are the heights of the
366 lower and upper boxes, respectively; $w_{t,L}$ is the exchange velocity between the lower and upper
367 boxes, and $w_{t,U}$ is the exchange velocity between the upper box and the overlying background

atmosphere; $\Delta S_{i,L}$ and $\Delta S_{i,U}$ are chemical sources of i^{th} species in the lower and upper boxes, respectively; and $E_{i,L}$ is emission rates of i^{th} species.

Exchange velocities implemented into the two-box model are determined from the current LES model by calculating the ventilation of a passive scalar, i.e. $w_{t,L} = \frac{F_L}{c_{ps,L} - c_{ps,U}}$ and $w_{t,U} = \frac{F_U}{c_{ps,U} - c_{ps,b}}$, where F_L is the flux between the lower and upper boxes, F_U is the flux between the upper box and the overlying background atmosphere and ‘ps’ denotes the passive scalar. The resulting values applied into the two-box model are 0.018 m s^{-1} for $w_{t,L}$ and 0.014 m s^{-1} for $w_{t,U}$. The two-box model is then compared with the LES model in terms of the time evolution of the volume averaged mixing ratios of NO, NO₂, O₃, NO_x and O_x (see Fig. 8). There are apparent fluctuations in the mixing ratios of chemical species inherent in the LES approach due to dynamically-driven variability of large scale eddies and unsteady ventilation caused by the two primary vortices in the canyon. The two-box model generally matches the LES approach with respect to the mixing ratios for the lower box, but slightly underestimates for the upper box compared with the LES results. This may attributed to the greater mixing for the lower vortex than that for the upper vortex in the LES, indicated by the very small values for the PSS defects (Fig. 4g and Fig. 5g).

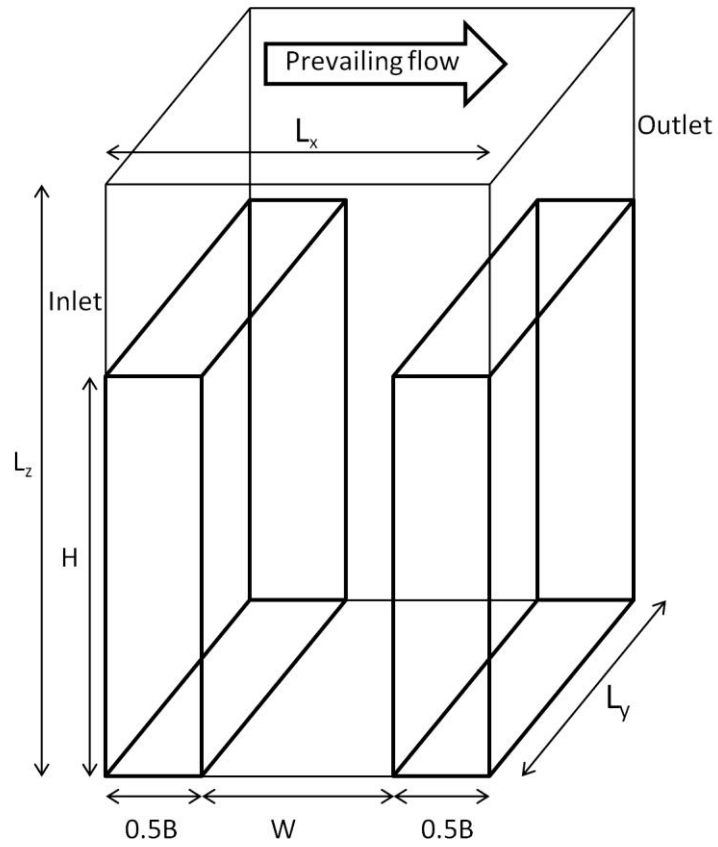
4 Conclusions

The dispersion and transport of reactive pollutants in a deep urban street canyon (AR=2) has been examined using an LES model coupled with simple NO_x-O₃ photochemistry. It is observed that there exist two vertically aligned vortices, agreeing reasonably well with a previous water channel experiment. Reactive pollutants exhibit significant spatial variation caused by the two unsteady vortices. Ground level sourced pollutants (NO_x) are found to be largely trapped within the lower

390 vortex with a maximum value of about 1100 ppb. The deviation from chemical equilibrium in the
391 upper vortex is much greater than that in the lower vortex. Imperfect mixing (reflected in non-zero
392 values for the PSS defect) results in negative apparent chemical ozone production, representing a
393 systematic error if such an approach is applied to obtain ozone production rates within a poorly-
394 mixed environment close to NO_x emissions sources. The substantial magnitude of the apparent
395 ozone loss rate, relative to those encountered in the wider boundary layer / free troposphere, further
396 suggests that even at some distance from fresh emissions, mixing-derived PSS defects may limit
397 this approach in inferring chemical ozone production. This study demonstrates an approach to
398 quantify parameters for a simplified two-box model, which could support traffic management and
399 urban planning strategy or personal exposure assessment. A challenging research task for future
400 study is to incorporate complex chemical mechanisms and consider various aspect ratios and wind
401 speeds.

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408 Fig. 1 Schematic diagram of the computational domain where $L_x=36$ m, $L_y=40$ m and $L_z=112$ m. H ($=36$ m) is the
 409 building height, W ($=18$ m) is the street width and B ($=18$ m) is the building width.

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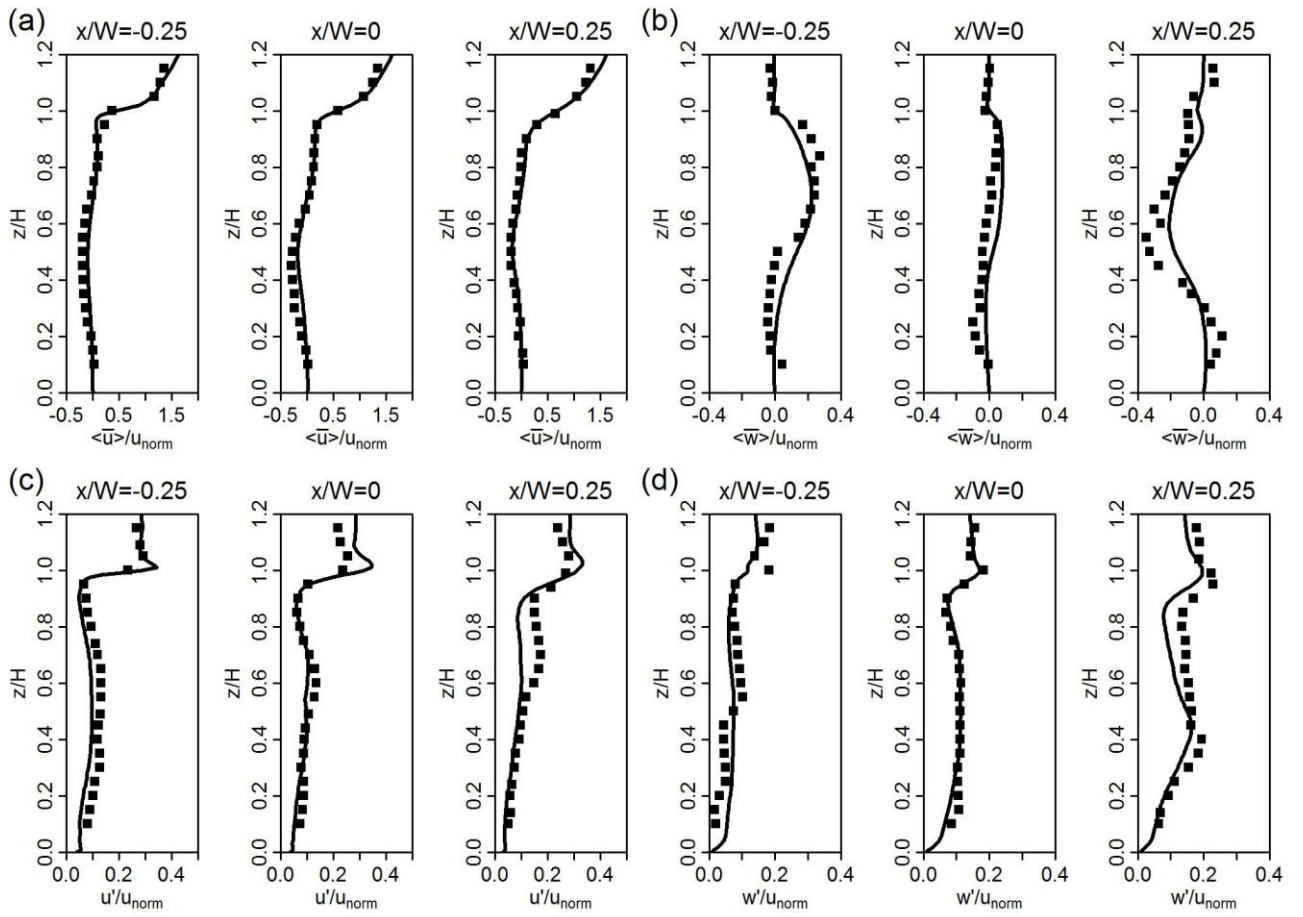


Fig 2. Comparison of the vertical profiles of the normalized averaged streamwise and vertical velocities and their fluctuations at the upstream ($x/W = -0.25$), centre ($x/W = 0$) and downstream position ($x/W = 0.25$) for the deep street canon with an aspect ratio of 2: (a) $\langle \bar{u} \rangle / u_{norm}$, (b) $\langle \bar{w} \rangle / u_{norm}$, (c) u' / u_{norm} and (d) w' / u_{norm} . Solid lines represent the current LES simulation; Dark squares denote the water-channel experiment carried out by Li et al. (2008a).

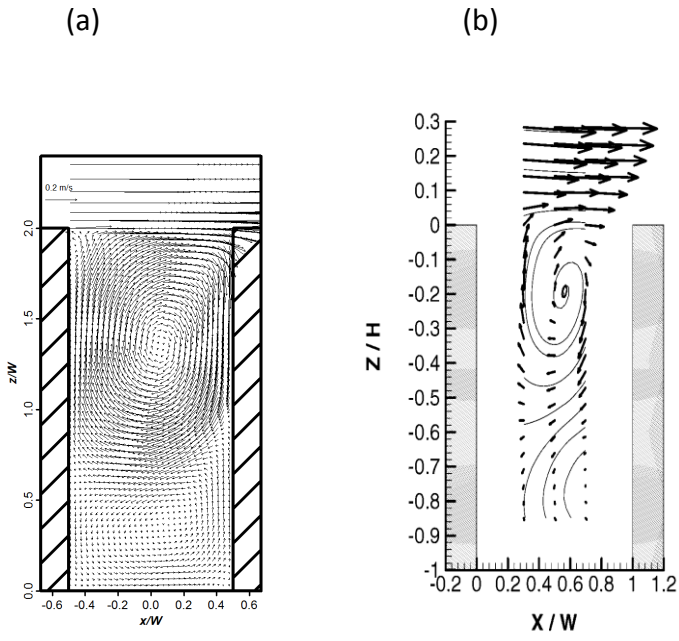


Fig 3. Vortex structure in the (a) current LES simulation (b) wind tunnel experiment carried out by (Kovar-Panskus et al., 2002).

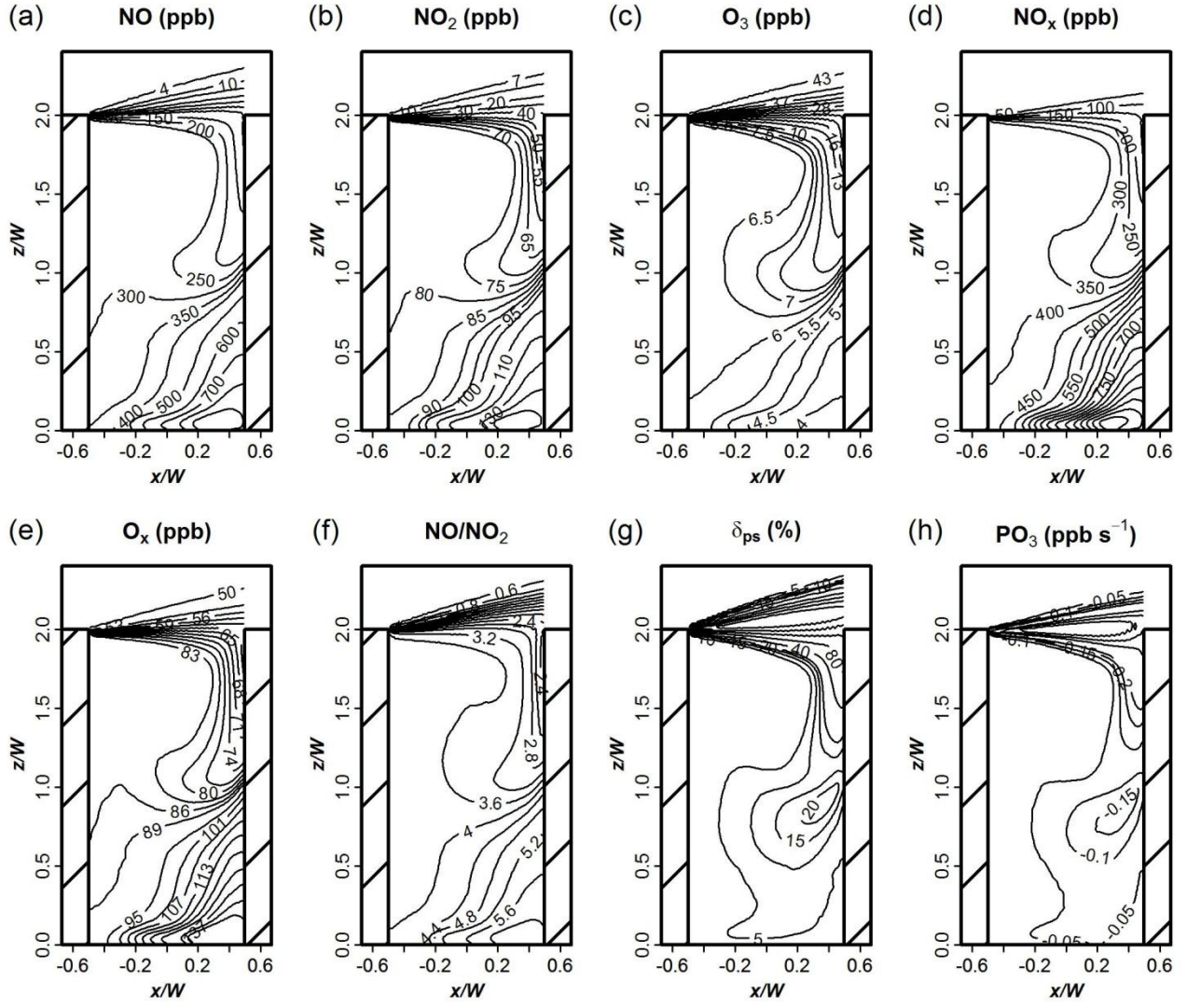


Fig. 4 Contour plots of the spatially and temporally averaged [see Equation (23)] (a) $\langle \overline{NO} \rangle$, (b) $\langle \overline{NO_2} \rangle$, (c) $\langle \overline{O_3} \rangle$, (d) $\langle \overline{NO_x} \rangle$, (e) $\langle \overline{O_x} \rangle$, (f) $\langle \overline{NO} \rangle / \langle \overline{NO_2} \rangle$, (g) d_{ps} and (h) PO_3 .

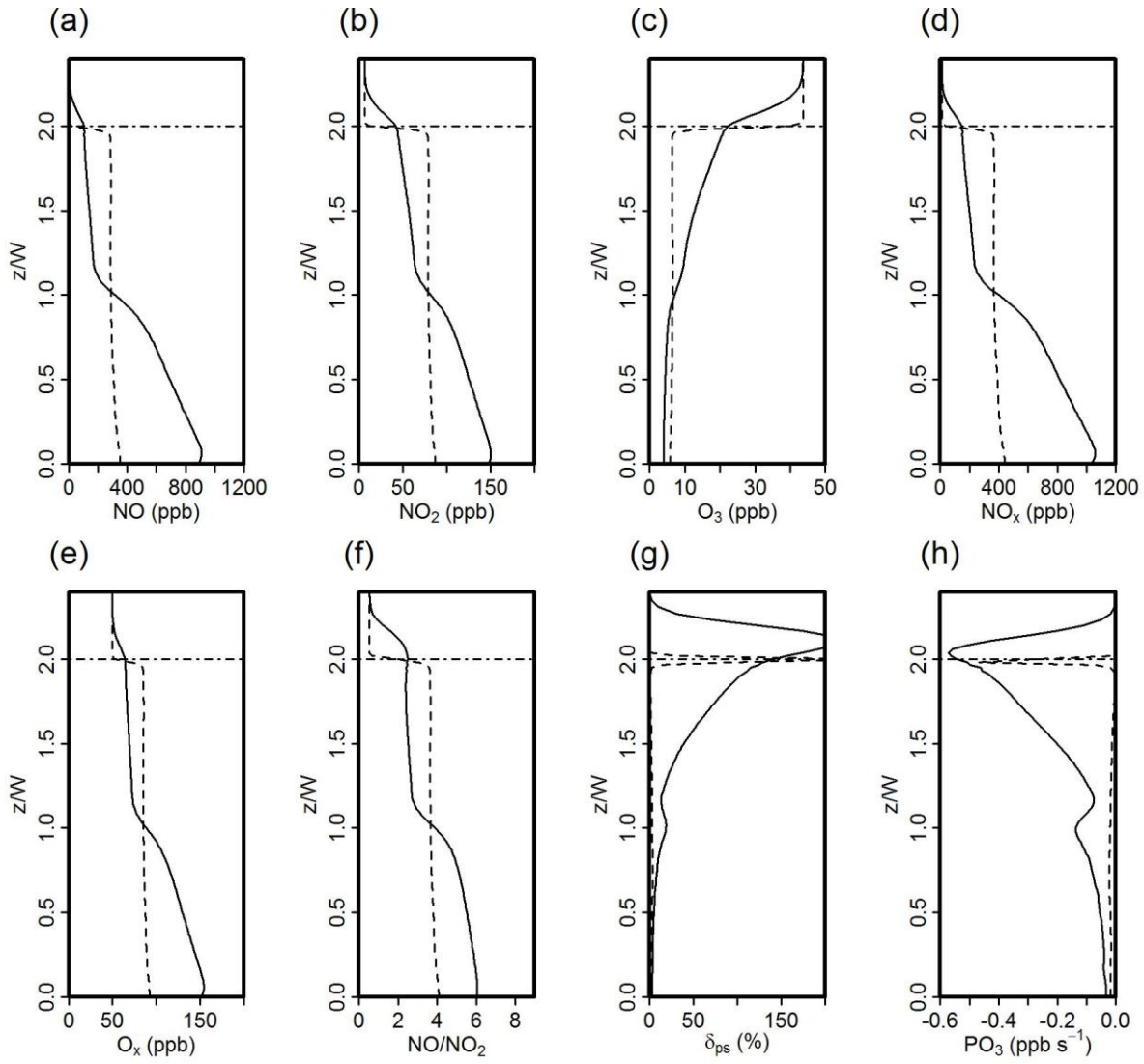


Fig. 5 Vertical profiles of the spatially and temporally averaged [see Equation (23)] (a) $\langle \overline{NO} \rangle$, (b) $\langle \overline{NO_2} \rangle$, (c) $\langle \overline{O_3} \rangle$, (d) $\langle \overline{NO_x} \rangle$, (e) $\langle \overline{O_x} \rangle$ and (f) $\langle \overline{NO} \rangle / \langle \overline{NO_2} \rangle$, (g) d_{ps} and (h) PO_3 along the leeward wall represented by the dash lines, and along the windward wall represented by the solid lines.

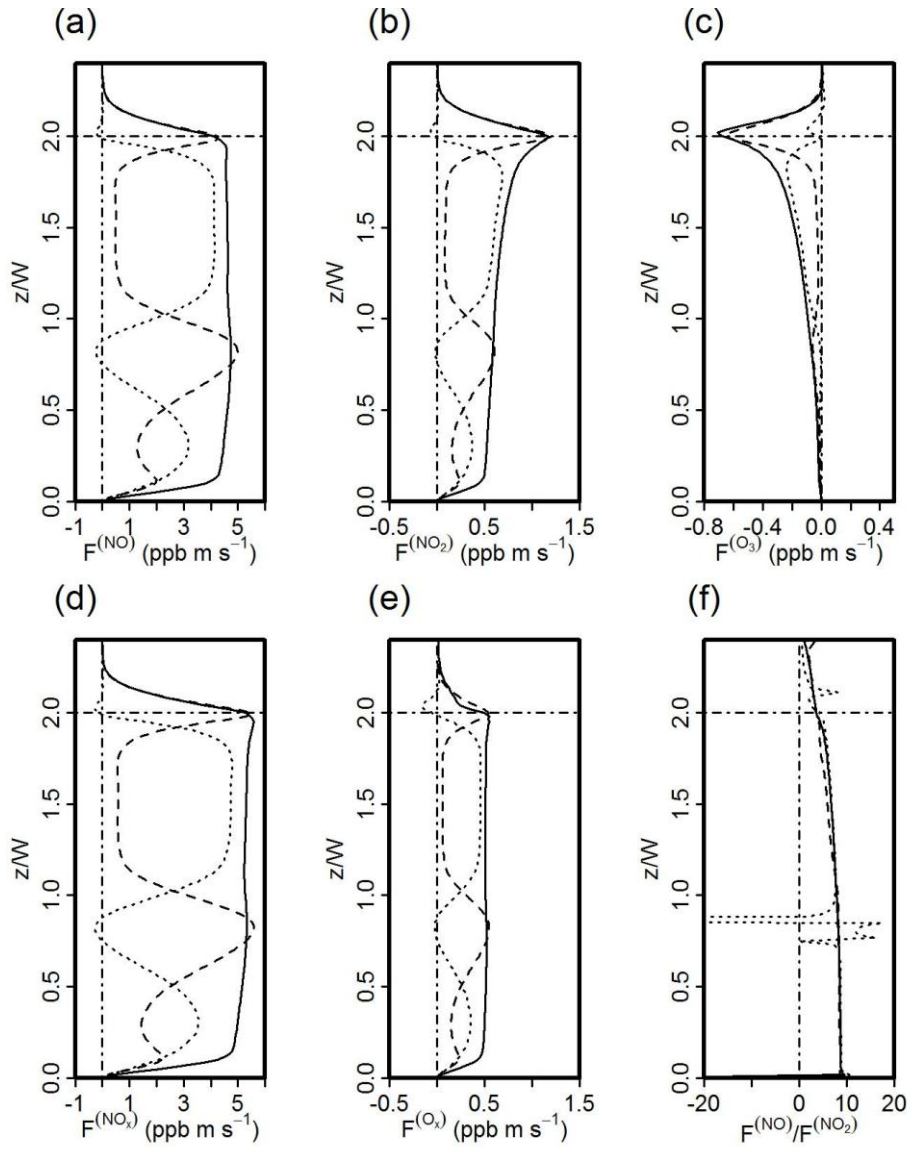
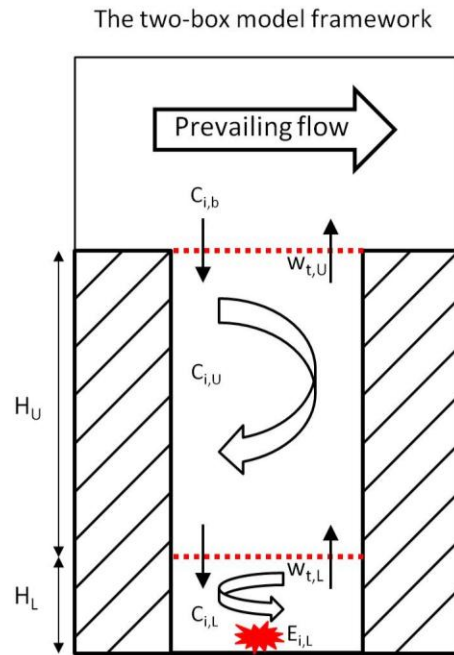


Fig. 6 Vertical profiles of the spatially and temporally averaged total, turbulent and advective fluxes for (a) NO, (b) NO₂, (c) O₃, (d) NO_x, (e) O_x and (f) NO/NO₂ averaged across the canyon. The total, turbulent and advective fluxes for each quantity are represented by the solid, dash and dotted lines, respectively.



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473 Fig. 7 Sketch of the two-box model framework. $C_{i,L}$ (ppb), $C_{i,U}$ (ppb) and $C_{i,b}$ (ppb) are the concentrations of i^{th}
 474 species ($i=\text{NO}, \text{NO}_2$ and O_3) in the lower box, upper box, and overlying background atmosphere, respectively; H_L (m)
 475 and H_U (m) are the height of the lower and upper boxes, respectively; $w_{t,L}$ (m s^{-1}) is the exchange velocity between
 476 the lower and upper boxes, and $w_{t,U}$ (m s^{-1}) is the exchange velocity between the upper box and the overlying
 477 background atmosphere; and $E_{i,L}$ (ppb s^{-1}) is the emission rates of i^{th} species.

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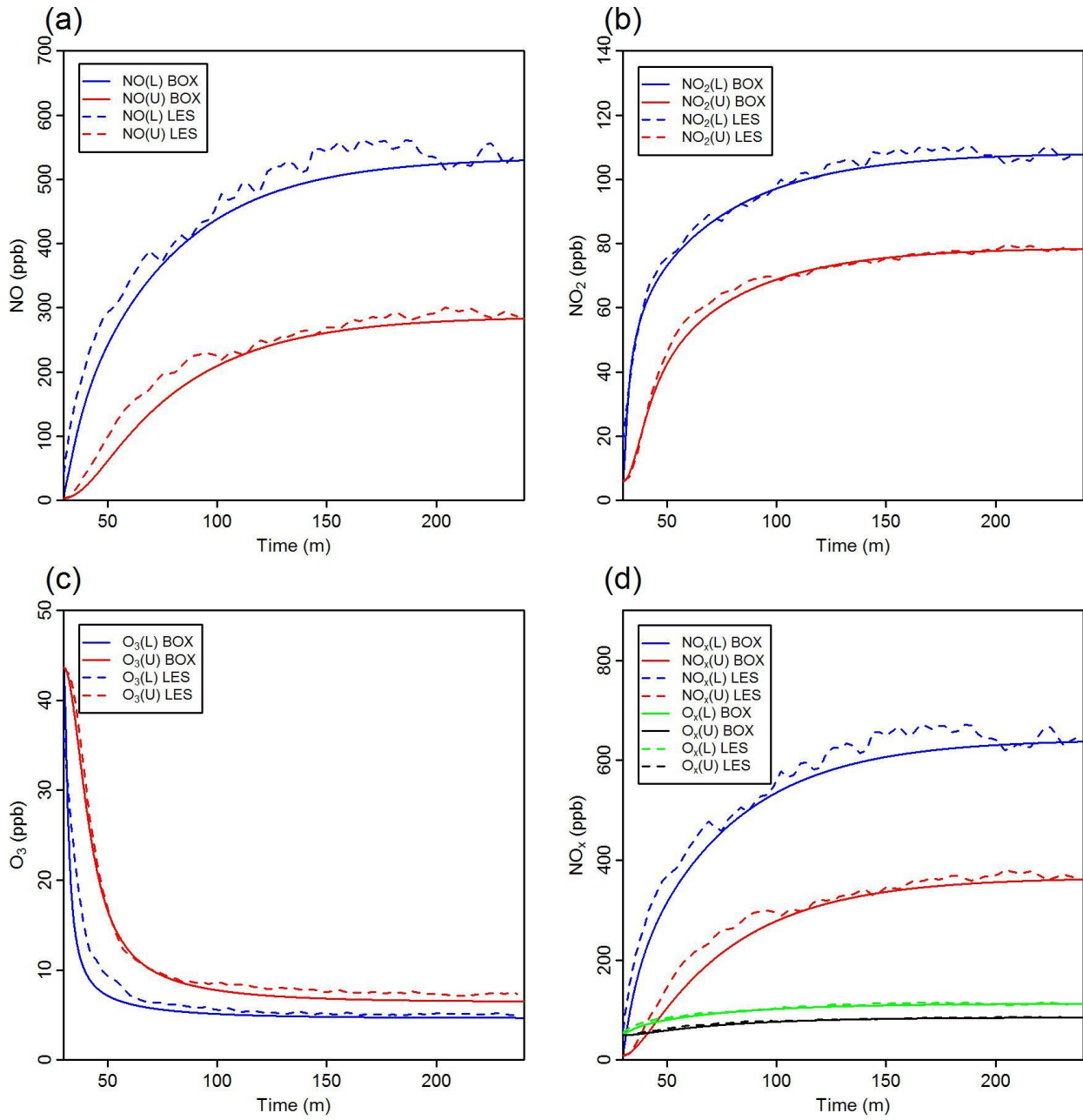


Fig. 8 Time evolution of the volume averaged mixing ratios of (a) NO, (b) NO₂, (c) O₃ and (d) NO_x and O_x calculated using the LES simulation (LES) and the two-box model (BOX), respectively. 'L' represents the lower box while 'U' represents the upper box.

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